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me to the best of my knowledge and belief of the following Japanese patent application:  
Japanese Patent Application No. JP 2003-063205 filed March 10, 2003.

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Michio Ogawa

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Signature of Translator



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[Inventor]

[Address or Residence] c/o Kuraray Co., Ltd.,  
2-1, Kaigan-dori 1-chome,  
Okayama-shi, Okayama-ken

[Name] Hideki KAMADA

[Patent Applicant]

[Identification Number] 000001085

[Name or Appellation] Kuraray Co., Ltd.

[Representative] Yasuaki WAKUI

[Telephone Number] 03-3277-3182

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Specification

[Title of the Invention]

POLYVINYL ALCOHOL BINDER FIBERS

[Claims]

[Claim 1] Polyvinyl alcohol binder fibers having a cross-section circularity of at most 35 %, a degree of swelling in water at 30°C of at least 100 %, and a degree of dissolution therein of at most 20 %.

[Claim 2] Polyvinyl alcohol binder fibers as claimed in claim 1, which have a flattened cross-sectional profile, and satisfy  $A/B \geq 3$  and  $0.6 \leq C/B \leq 1.2$  where A indicates the length of the major side of the cross section, B indicates the thickness of the center ( $1/2A$ ) of the major side, and C indicates the thickness of the part of  $1/4A$  from the end of the major side.

[Claim 3] Polyvinyl alcohol binder fibers as claimed in claim 2, wherein the thickness B of the center ( $1/2A$ ) of the major side of the cross section is at most 6  $\mu\text{m}$ .

[Claim 4] Polyvinyl alcohol binder fibers as claimed in any one of claims 1 to 3, wherein the polyvinyl alcohol resin is copolymerized with from 0.1 to 15 mol% of any of a carboxylic acid group, a sulfonic acid group, an ethylene group, a silane group, a silanol group, an amine group and an ammonium group.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to polyvinyl alcohol binder

fibers capable of melting under low-energy drying condition, for example, in high-speed drying in a hot air drying system or in low-temperature drying in a multi-cylinder system or the like, and capable of giving paper and nonwoven fabrics of high strength.

[0002]

[Prior Art]

At present, polyvinyl alcohol (hereinafter abbreviated to PVA) fibers are used as binder fibers in papermaking, as they are soluble in water and their adhesiveness is high. The adhesiveness of PVA binder fibers is high, and this is because the fibers swell in water where they have dispersed in a step of papermaking with them, and may therefore well melt under heat in a step of drying them, and they crystallize while being dried.

Heretofore when PVA fibers are used in producing paper or nonwoven fabrics, a thermal drum-type Yankee drier is generally used in the step of drying them. The Yankee drier generates a large quantity of heat for drying, and therefore when PVA binder fibers are dried therein, they may well melt and express high adhesiveness. However, with the recent tendency in the art toward efficient drying and improved productivity, air-through driers and the like have become much used in many cases, but they are problematic in the following point. When air-through driers are driven for drying therein, they have a short drying time and generate a small quantity of

drying heat, and therefore ordinary PVA binder fibers could not well melt while dried therein, and, as a result, the dried fibers could not express sufficient adhesiveness.

[0003]

To solve the problem as above, various methods have been employed. For example, PVA resin having a low degree of saponification is used for the starting material; or an ionic functional group, for example, a cationic group such as carboxyl group, sulfonic acid group, silyl group or quaternary ammonium group is introduced into PVA resin to thereby improve the solubility of the resulting resin.

For example, the degree of saponification of PVA resin is lowered so as to increase the solubility of the resin, and the degree of polymerization of PVA resin is lowered so as to increase the solubility of the resin, and various methods for these have been proposed (refer to Patent References 1, 2). Another technique has also been proposed, which comprises introducing a silyl group, a carboxyl group or an ethylene group into PVA resin to thereby increase the solubility and the adhesiveness of the resin (refer to Patent References 3, 4, 5, 6).

In related art as in the above, modification of PVA resin is essentially investigated for attaining increased adhesiveness of binder fibers. The cross-sectional profile of the binder fibers is roundish or cocoon-shaped, and the

cross-section circularity thereof is 37 % or more.

[0004]

[Patent Reference 1]      JP-A 51-96533

[Patent Reference 2]      JP-A 51-96534

[Patent Reference 3]      JP-A 60-231816

[Patent Reference 4]      JP-A 4-126818

[Patent Reference 5]      JP-A 58-220806

[Patent Reference 6]      JP-A 2003-27328

[0005]

[Problems that the Invention is to Solve]

We, the present inventors have assiduously studied for the purpose of solving the problems mentioned above, and, as a result, have found that, when the cross-section circularity of binder fibers is controlled to be at most 35 %, then the surface area of the fibers can be increased and the fibers can express high paper strength even though they are dried under low-energy drying condition, for example, in high-speed drying in a hot air drying system or in low-temperature drying in a multi-cylinder system.

[0006]

[Means for Solving the Problems]

Specifically, the invention is polyvinyl alcohol binder fibers having a cross-section circularity of at most 35 %, a degree of swelling in water at 30°C of at least 100 %, and a degree of dissolution therein of at most 20 %.

[0007]

[Mode for Carrying out the Invention]

A most efficient method for controlling the cross-section circularity to at most 35 % is to make the fibers have a flattened cross-sectional profile. Preferably, as in Fig. 1, the fibers satisfy  $A/B \geq 3$  and  $0.6 \leq C/B \leq 1.2$  where A indicates the length of the major side of the flattened cross section, B indicates the thickness of the center ( $1/2A$ ) of the major side, and C indicates the thickness of the part of  $1/4A$  from the end of the major side. More preferably, B is at most 6  $\mu\text{m}$ , and the adhesion efficiency of the fibers is further increased in the case.

Needless-to-say, the polyvinyl alcohol resin may be copolymerized with any one or more of a carboxylic acid group, a sulfonic acid group, an ethylene group, a silane group, a silanol group, an amine group and an ammonium group, like in the related art.

[0008]

The adhesiveness of PVA binder fibers is high, and this is because the fibers swell in water where they have dispersed in a step of papermaking with them, and may therefore well melt under heat in a step of drying them, and they crystallize while being dried. However, conventional PVA binder fibers could not well melt under low-energy drying condition, for example, in trendy high-speed drying or low-temperature drying, and therefore could not be highly adhesive when dried under such

condition. In conventional techniques, the degree of saponification of PVA resin is lowered or a modified group is introduced into PVA resin to thereby lower the crystal size of the resin, as so mentioned hereinabove. This is for lowering the crystal-melting temperature of the resin as an index of the resolvability of the resin. Different from it, the invention is characterized in that the cross-section circularity of fibers is significantly lowered and the adhesive area thereof is increased so as to increase the strength of paper made with the fibers.

The cross-section circularity of the PVA binder fibers of the invention is at most 35 %, but preferably from 5 to 30 %, more preferably from 20 to 30 %. Regarding the factors of the flattened cross-sectional profile of the fibers, it is desirable that  $0.6 \leq C/B \leq 1.2$ . If  $C/B < 0.6$  or  $C/B > 1.2$ , then the area of the contact point of the binder fibers may lower and the fibers could not express an efficient binder effect. Preferably,  $0.8 \leq C/B \leq 1.2$ , more preferably  $0.9 \leq C/B \leq 1.1$ .  
[0009]

The degree of swelling in water at 30°C of the binder fibers of the invention must be at least 100 %. If the degree of swelling thereof is smaller than 100 %, then the fibers could not fully express the potency as binder. Preferably, it is at least 120 %.

[0010]



The polyvinyl alcohol resin for use in the invention is not specifically defined. For example, it may be low-saponification PVA, or PVA copolymerized with any of a carboxyl acid group, a sulfonic acid group, an ethylene group, a silane group, a silanol group, an amine group and an ammonium group. The degree of dissolution of the fibers in water at 30°C must be at most 20 %. If their dissolution therein is over 20 %, then the yield in papermaking with the fibers is low and therefore the cost of the products increases. If so, in addition, the fibers will dissolve in white water (water used in papermaking) to increase the drainage load in papermaking, and, when the fibers are used in papermaking, the dissolved PVA will re-adhere to the paper products produced to thereby worsen the paper quality (concretely, the paper feel will be rough and hard). Preferably, the fiber dissolution is at most 10 %, more preferably at most 5 %.

[0011]

Though not specifically defined, the single-fiber mean fineness of the PVA binder fibers of the invention may generally fall between 0.01 and 50 dtex. If the mean fineness is smaller than 0.01 dtex, then the fibers will be difficult to produce and therefore the productivity of the fibers will lower and the production costs thereof will increase. On the other hand, if the mean fineness is larger than 50 dtex, then the fiber diameter of the single fibers increases and therefore the adhesiveness

of the fibers will be poor. Preferably, the mean fineness falls between 0.1 and 5.0 dtex. The fibers of the invention may be used in any form. For example, they may be cut fibers, filament yarns or spun yarns.

[0012]

The degree of polymerization of the PVA resin for use in the invention is preferably at least 300 in point of the dissolution of the resin, but preferably at most 3000 in point of the productivity and the cost of the resin. More preferably, it falls between 800 and 2000. The degree of saponification of PVA for use herein is preferably at least 95 mol% in point of the dissolution of PVA. If the degree of saponification thereof is smaller than 95 mol%, then PVA dissolves too much while the binder formed of it is used and therefore causes some problems in that the yield of the polymer is low and the polymer dissolves in exhaust water. If so, in addition, the water resistance of the binder formed of it is extremely low, and the binder potency is extremely poor in wet condition. More preferably, the degree of saponification of PVA falls between 96 and 99.9 mol%.

[0013]

The PVA binder fibers of the invention may be produced by dissolving the above-mentioned PVA resin in water to prepare a spinning solution having a polymer concentration of from 8 to 18 % by weight, then spinning it into fibers in a coagulation

bath that contains an aqueous solution of a salt having the ability to coagulate the polymer, drawing the fibers by 2 to 5 times in wet, and drying them. If the concentration of the PVA resin dissolved in water is lower than 8 % by weight, then the spinning solution could not be rapidly coagulated when it is spun into a coagulation bath and, if so, the single fibers formed may adhere to each other and their dispersibility may be poor. This reduces the productivity and increases the production cost. On the other hand, if the concentration of the PVA resin dissolved in water is higher than 18 % by weight, then the viscosity of the resulting PVA polymer solution will be too high and the polymer solution could not be spun into fibers. Preferably, the polymer concentration falls between 10 and 16 % by weight.

[0014]

The salt to form an aqueous solution thereof having the ability to coagulate the resin includes sodium sulfate (Glauber's salt), ammonium sulfate and sodium carbonate. The fibers formed in the coagulation bath that contains an aqueous solution of the salt having the ability to coagulate the resin are then drawn in wet. In this stage, if the wet draw ratio is smaller than 2 times, then the fibers could not be spun suitably. However, if the wet draw ratio is larger than 5 times, then the PVA molecules will be too much oriented and the crystal melting temperature of the resulting fibers will therefore

increase. If so, the degree of swelling in water of the fibers thus obtained lowers and the fibers could not serve as binder.

[0015]

Paper and nonwoven fabrics are produced by the use of the PVA binder fibers obtained according to the above-mentioned production method. Preferably, the content of the PVA binder fibers in the paper and nonwoven fabrics produced is from 1 to 50 % by weight of the overall solid content of the fibrous products. If the content of the PVA binder fibers in the paper and nonwoven fabrics produced is lower than 1 % by weight, then the fibers could not act as binder since the number of the constitutive fibers in the fibrous products is small, and the fibers could not express adhesiveness. On the other hand, if the content of the PVA binder fibers in the paper and nonwoven fabrics produced is higher than 50 % by weight, then it means that the binder fibers are the main ingredient of the fibrous products. If so, the shrinkage of the binder fibers in the fibrous products, paper and nonwoven fabrics may lower the surface smoothness of the fibrous products and roughen the feel thereof, or that is, it may worsen the quality of the fibrous products. More preferably, the content of the PVA binder fibers falls between 2 and 30 % by weight, even more preferably between 5 and 25 % by weight.

[0016]

[Examples]

The invention is described with reference to the following Examples, which, however, are not intended to restrict the scope of the invention. In the invention, the degree of polymerization of the PVA resin; the degree of dissolution and the degree of swelling of the PVA binder fibers; and the wet breaking length (WB) and the dry breaking length (DB) of the paper produced by the use of the PVA binder fibers of the invention are measured according to the methods described below.

[0017]

[Cross-Section Circularity]

The cross-section circularity of the fibers is obtained according to the following formula:

$$\text{Cross-Section Circularity (\%)} = (A/B) \times 100,$$

in which A indicates the cross-section area of a fiber, and B indicates the minimum circle area that surrounds the fiber.

[0018]

[Degree of Polymerization of PVA]

A PVA polymer is dissolved in hot water to have a polymer concentration of from 1 to 10 g/liter (Cv), and the relative viscosity  $\eta_{rel}$  of resulting polymer solution is measured at 30°C according to JIS K6726. The intrinsic viscosity  $[\eta]$  of the polymer is obtained according to the following formula (1), and the degree of polymerization PA thereof is calculated according to the following formula (2).

$$[\eta] = 2.303 \cdot \log(\eta_{rel}) / C_v \quad (1),$$

$$PA = ([\eta] \times 104 / 8.29) \times 1.613 \quad (2).$$

[0019]

#### [Determination of PVA Dissolution from PVA Binder Fibers]

The fibers are sampled to prepare a sample thereof having a pure PVA resin content of 1 g, and it is dipped in 100 ml of water at 30°C and statically kept therein for 30 minutes still at 30°C. After thus kept, the insoluble part is removed and 50 ml of the supernatant is collected. This is evaporated on a steam bath to dryness, and then further dried in a drier at 105°C for 4 hours. After thus dried, the dried residue a (g) is weighed. The dried residue contains PVA and inorganic matter such as sodium sulfate, and it is fired at 500 to 800°C until the PVA component is completely removed. After thus fired, the residue b (g) is weighed. The PVA dissolution is obtained according to the following formula:

$$\text{PVA Dissolution (\%)} = (a - b) \times 200.$$

[0020]

#### [Degree of Swelling of PVA Binder Fibers]

The fibers are sampled to prepare a sample thereof having a pure PVA resin content of 1 g, and it is dipped in 100 ml of water at 30°C and statically kept therein for 30 minutes still at 30°C. After thus kept, the fibers are taken out through filtration and dewatered in a centrifugal dewatering machine at 3000 rpm for 10 minutes, and the weight (A) of the dewatered

fibers is measured. After its weight has been measured, the sample is dried in a hot air drier at 105°C for 4 hours, and its weight (B) is again measured. The degree of swelling of the fibers is obtained according to the following formula:

$$\text{Degree of Swelling (\%/PVA)} = [(A - B)/B] \times 100.$$

[0021]

[Wet Breaking Length WB, Dry Breaking Length DB]

The fibers of the following Examples 1 to 4 and Comparative Examples 1 to 3 are cut into 3-mm pieces. 20 parts by weight of the fibers in terms of the pure fiber content, and 80 parts by weight of glass fibers (fiber diameter 9  $\mu\text{m}$ , fiber length 6 mm) are uniformly mixed and stirred to prepare a slurry. The resulting slurry is fed into a TAPPI papermaking machine and formed into paper. This is dried on a net-type air-through drier at a drying temperature of 210°C, and the paper thus obtained has a weight of 40 g/m<sup>2</sup>. The dry breaking length DB of the paper is measured as follows: The paper is conditioned in a room at 23°C and 50 % RH for 24 hours, and then cut into a sample having a width of 15 mm and a length of 170 mm. The dry strength DS (N) of the sample is measured at a pulling rate of 50 mm/min. The sample holding length is 100 mm. The dry breaking length DB of the paper is obtained according to the following formula, in which W (g/m<sup>2</sup>) indicates the weight of the sample.

$$\text{DB (dry breaking length)} = \text{DS}/(15 \times W) \times 1000 \text{ (N}\cdot\text{m/g)}.$$

The wet breaking length WB of the paper is measured as follows: The paper is dipped in water at 20°C for 24 hours to thereby make it absorb water, and this is then cut into a sample having a width of 15 mm and a length of 170 mm. The wet strength WS (N) of the sample is measured at a pulling rate of 50 mm/min. The sample holding length is 100 mm. The wet breaking length WB of the paper is obtained according to the following formula, in which W (g/m<sup>2</sup>) indicates the weight of the sample.

$$WB \text{ (wet breaking length)} = WS / (15 \times W) \times 1000 \text{ (N}\cdot\text{m/g)}.$$

[0022]

[Example 1]

An aqueous spinning solution of 14 % by weight of PVA resin having a mean degree of polymerization of 1700 and a degree of saponification of 98.0 mol% was spun out into a coagulation bath of saturated sodium sulfate, through a spinneret with 4000 rectangular slit orifices of 30  $\mu\text{m}$  (length)  $\times$  180  $\mu\text{m}$  (width), and the resulting fibers were wound up around a first roller, and then drawn in wet by 4 times. Then, these were dried in a constant-length drier at 120°C for 10 minutes to be flattened PVA fibers having a fineness of 1.5 dtex. Its data are given in Table 1.

[0023]

[Example 2]

An aqueous spinning solution of 14 % by weight of PVA resin having a mean degree of polymerization of 1700, a degree of



saponification of 98.0 mol% and an ethylene content of 5 mol% was spun out into a coagulation bath of saturated sodium sulfate, through a spinneret with 4000 rectangular slit orifices of 30  $\mu\text{m}$  (length)  $\times$  180  $\mu\text{m}$  (width), and the resulting fibers were wound up around a first roller, and then drawn in wet by 4 times. Then, these were dried in a constant-length drier at 120°C for 10 minutes to be flattened PVA fibers having a fineness of 1.5 dtex. Its data are given in Table 1.

[0024]

[Example 3]

An aqueous spinning solution of 14 % by weight of PVA resin having a mean degree of polymerization of 1700 and a degree of saponification of 99.9 mol% was spun out into a coagulation bath of saturated sodium sulfate, through a spinneret with 4000 rectangular slit orifices of 30  $\mu\text{m}$  (length)  $\times$  180  $\mu\text{m}$  (width), and the resulting fibers were wound up around a first roller, and then drawn in wet by 4 times. Then, these were dried in a constant-length drier at 120°C for 10 minutes to be flattened PVA fibers having a fineness of 1.5 dtex. Its data are given in Table 1.

[0025]

[Example 4]

An aqueous spinning solution of 14 % by weight of PVA resin having a mean degree of polymerization of 1700 and a degree of saponification of 98.0 mol% was spun out into a coagulation bath

of saturated sodium sulfate, through a spinneret with 4000 rectangular slit orifices of 30  $\mu\text{m}$  (length)  $\times$  450  $\mu\text{m}$  (width), and the resulting fibers were wound up around a first roller, and then drawn in wet by 4 times. Then, these were dried in a constant-length drier at 120°C for 10 minutes to be flattened PVA fibers having a fineness of 3.8 dtex. Its data are given in Table 1.

[0026]

[Example 5]

An aqueous spinning solution of 14 % by weight of PVA resin having a mean degree of polymerization of 1700 and a degree of saponification of 98.0 mol% was spun out into a coagulation bath of saturated sodium sulfate, through a spinneret with 4000 rectangular slit orifices of 30  $\mu\text{m}$  (length)  $\times$  180  $\mu\text{m}$  (width), and the resulting fibers were wound up around a first roller, and then drawn in wet by 4 times. Then, these were washed in water at 15 to 30°C under a constant length condition, and thereafter dried in a constant-length drier at 120°C for 10 minutes to obtain salt-free, flattened PVA fibers having a fineness of 1.5 dtex. Its data are given in Table 1.

[0027]

[Example 6]

A spinning solution in DMSO (dimethylsulfoxide) of 18 % by weight of PVA resin having a mean degree of polymerization of 1700 and a degree of saponification of 98.0 mol% was spun

out into a coagulation bath of methanol, through a spinneret with 20000 rectangular slit orifices of 30  $\mu\text{m}$  (length)  $\times$  180  $\mu\text{m}$  (width), and the resulting fibers were wound up around a first roller, and then drawn in wet by 3 times. Then, these were dried in a constant-length drier at 140°C for 10 minutes to obtain salt-free, flattened PVA fibers having a fineness of 2.2 dtex. Its data are given in Table 1.

[0028]

[Comparative Example 1]

An aqueous spinning solution of 14 % by weight of PVA resin having a mean degree of polymerization of 1700 and a degree of saponification of 99.9 mol% was spun out into a coagulation bath of saturated sodium sulfate, through a spinneret with 4000 circular orifices of 60  $\mu\text{m}$  (diameter), and the resulting fibers were wound up around a first roller, and then drawn in wet by 4 times. Then, these were dried in a constant-length drier at 120°C for 10 minutes to be cocoon-shaped PVA fibers having a fineness of 1.0 dtex. Its data are given in Table 1.

[0029]

[Comparative Example 2]

An aqueous spinning solution of 14 % by weight of PVA resin having a mean degree of polymerization of 1700 and a degree of saponification of 98.0 mol% was spun out into a coagulation bath of saturated sodium sulfate, through a spinneret with 4000 circular orifices of 60  $\mu\text{m}$  (diameter), and the resulting fibers

were wound up around a first roller, and then drawn in wet by 4 times. Then, these were dried in a constant-length drier at 120°C for 10 minutes to be cocoon-shaped PVA fibers having a fineness of 1.0 dtex. Its data are given in Table 1.

[0030]

[Comparative Example 3]

Nichibi's Solvron "NL 2003" having a dumbbell-shaped cross-sectional profile was used, and its data are given in Table 1.

[0031]

[Table 1]

	Cross-section Circularity (%)	A/B	C/B	B ( $\mu$ m)	Degree of Swelling (%/P)	Degree of Dissolution (%)	DB (N·m/g)	WB (N·m/g)
Example 1	23	6.3	0.97	4.5	182	6.9	4.59	0.34
Example 2	23	6.1	0.97	4.5	154	2.3	4.63	0.78
Example 3	23	6.2	0.99	4.4	143	0.9	2.80	0.38
Example 4	9	16	0.98	4.5	162	3.1	4.48	0.35
Example 5	23	6.1	0.97	4.4	160	1.1	4.22	0.33
Example 6	25	5.5	0.95	4.7	170	3.3	4.32	0.34
Comparative Example 1	39	-	-	-	145	1.0	0.35	0.05
Comparative Example 2	39	-	-	-	162	3.1	1.52	0.29
Comparative Example 3	43	3.7	1.4	7.1	160	10	1.81	0.01

[0032]

[Advantages of the Invention]

The polyvinyl alcohol binder fibers of the invention have

a single-fiber cross-section circularity of at most 35 %, a degree of swelling in water at 30°C of at least 100 % and a degree of dissolution therein of at most 20 %, and these can be processed even under low-energy drying condition, for example, in high-speed drying in a hot air drying system or in low-temperature drying in a multi-cylinder system or the like to give paper and nonwoven fabrics of high strength.

[Brief Description of the Drawing]

[Fig. 1] It is a schematic view graphically showing cross-sectional profiles of flattened fibers.

[Designation of Document]      Abstract

[Abstract]

[Problem] To provide polyvinyl alcohol binder fibers capable of expressing high paper strength even when processed under low-energy drying condition, for example, in high-speed drying equipment such as a hot air drying system (air through drier) or in low-temperature drying equipment such as a multi-cylinder drying system.

[Means for Resolution] Polyvinyl alcohol binder fibers having a cross-section circularity of at most 35 %, a degree of swelling in water at 30°C of at least 100 %, and a degree of dissolution therein of at most 20 %.

[Selected Drawing] None